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Thermodynamics of Hydrogen-Bonding Mixtures 4.: G^E , H^E , S^E & C_p^E and Possible Double Azeotropy of Water + N-Methylethylenediamine

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ABSTRACT

An ebulliometer was used to measure total vapor-pressure (PTx) data on nine mixtures of water + N-methylethylenediamine (and the pure components) between 52° and 116°C. Bubble-point data were measured at six pressures from 13.33 kPa to 101.325 kPa. These PTx data indicate the following azeotropic behavior: at pressures below 32.7 kPa there is a single maximum-boiling azeotrope, above 46.7 kPa there is no azeotrope, and between 32.7 and 46.7 kPa there is the possibility of a double azeotrope. This type of double azeotrope is rare because the pure component vapor pressures are considerably different ($P_{\text{sat}1}/P_{\text{sat}2} \approx 1.6$); it may be that the apparent extrema in the Tx data are due to artifacts related to the purity of the N-methylethylenediamine (≈ 95 mass %).

A Redlich-Kister G^E model was fitted to isotherms at 60°, 85°, 90° and 100°C via Barker's method with an average standard error of 0.52 % in pressure. The system exhibits large negative deviations from ideality (derived $\gamma^\infty = 0.05 - 0.67$) which decrease with increasing temperature. Equimolar G^E/T values thus derived increase with increasing temperature which predicts a negative H^E . Equimolar C_p^E data, measured by differential scanning calorimetry (DSC), are positive and also increase with increasing temperature. These mixture thermodynamic data show that the system water + N-methylethylenediamine belongs to the class of mixtures where $G^E < 0$, $H^E < 0$, and $TS^E < 0$. Therefore the data indicate that (1-2) hydrogen-bonding of water with N-methylethylenediamine is greater than either the (1-1) or (2-2) hydrogen-bonding in the pure components.

INTRODUCTION

This paper presents PTx data and excess thermodynamic properties in a continuing study of hydrogen-bonding mixtures. No previous vapor-liquid equilibria or excess property data could be found for the system water + N-methylethylenediamine (Me-EDA; 1,2-ethanediamine, N-methyl-; CAS Registry No., 109-81-9). Comparisons are made to the system ethylenediamine (EDA) + water for which VLE data are available [1,2].

EXPERIMENTAL SECTION

The Me-EDA was Aldrich (95%) and the water was Aldrich (HPLC grade). These materials were used as received. Mixtures were prepared gravimetrically with analytical balances.

The ebulliometer has been described previously [3]. It is one-stage total-reflux boiler equipped with twin vapor-lift pumps to spray slugs of equilibrated liquid and vapor upon a thermometer well. A condenser cooled to 5°C provided connection to the manostat. Pressures were controlled with a Mensor Model 10205 quartz manostat/manometer to ± 0.007 kPa. Temperatures on the IPTS-68 scale were measured to $\pm 0.01^\circ\text{C}$ with a Hewlett-Packard Model 2804A quartz thermometer. Pure components and mixtures were charged to the ebulliometer and boiling points were measured [4] at 13.3, 26.7, 40.0, 53.3, 80.0 and 101.325 kPa.

Heat capacity data for the pure components and an equimolar mixture were measured with a SETARAM DSC-111G differential scanning calorimeter (DSC) by comparison to sapphire. The procedure was described by Stephens and Olson [5].

RESULTS

Table 1 contains 66 PTx measurements on the pure components and nine mixtures. The difference between x , the liquid-phase mole fraction and z , the overall mole fraction charged to the ebulliometer, shows the magnitude of the vapor-hold up and condensed vapor-holdup correction computed as described previously [6]. The PT data for each mixture were fit with a three-constant Antoine equation in order to interpolate isothermal Px data similar to the procedure described by Prengle and Palm [7]. The Antoine constants and derived Pxy data for 90°C are given in Table 2.

Values of G^E and y , the vapor-phase mole fraction, were computed by a Gauss-Newton nonlinear least-squares fit to the experimental mixture vapor pressures coupled with a bubble-point calculation during each iteration (Barker's method). The equation which describes thermodynamic equilibrium between the phases at T and P is,

$$\phi_i y_i P = x_i \gamma_i P_i^O \phi_i^O \exp[(P - P_i^O) V_i / (RT)] \quad i = 1, 2 \quad (1)$$

where ϕ is the vapor-phase fugacity coefficient, γ is the liquid-phase activity coefficient (reference state: pure liquid at system T and P), P_i^O is the pure-component vapor pressure, and V_i is the pure-component saturated-liquid molar volume. Saturated-liquid volume data were taken from the DIPPR databank [8] and the vapor-phase fugacity coefficients were computed from the second-virial equation of state. Second virial coefficients were estimated from the Hayden-O'Connell correlation [9].

The G^E model is the Redlich-Kister equation:

$$G^E = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \dots] \quad (2)$$

$$RT \ln \gamma_i = G^E + x_j (\partial G^E / \partial x_i)_{TP} \quad i, j = 1, 2 \quad (3)$$

where A, B, C, D, ... are parameters to be estimated in the least-squares fit.

Table 3 presents results from fitting the one-, two-, three-, and four-constant Redlich-Kister models to the derived P_x data at 90°C. The standard rms error from the least-squares fit is reduced with the addition of each of the four constants. The pressure residuals from the four-constant least-squares fit display no systematic trends. Derived P_x data at 60°, 85°, and 100°C were analyzed in a similar fashion to produce G^E data that could be used with the Gibbs-Helmholtz equation to predict H^E as described in the DISCUSSION section.

Table 4 contains molar heat capacity data (C_σ) for water, Me-EDA, and an equimolar mixture measured in the liquid + vapor (saturation) region between 25° and 80°C. At these low temperatures, $C_P \cong C_\sigma$. The last column of Table 4 contains equimolar C_P^E data computed from the measured mixture data. Figure 1 shows the C_σ data vs. temperature.

DISCUSSION

The precision (and accuracy if systematic errors are absent) of the PT_x data is indicated by the standard rms error in the Barker's method fit, $\approx 0.52\%$ in pressure. Heat capacity data measured by DSC in comparison to sapphire are accurate to about $\pm 1\text{-}2\%$.

The Gibbs-Helmholtz equation was used to derive enthalpy-of-mixing, H^E , data from the temperature dependence of the G^E data:

$$H^E = -T^2(\partial g/\partial T)_x \quad (4)$$

where $g = G^E/T$. Figure 2 shows equimolar g vs. T from analysis of our PTx data. The slope of the curve at 90°C gives an equimolar H^E of -4400 J/mol. Because H^E is derived by differentiation, experimental error is magnified. It is possible this derived equimolar H^E is correct in sign at 90°C but that the actual H^E is lower in magnitude as was found for 1,2-propylene glycol + ethylene glycol [10].

The equimolar excess thermodynamic functions at 90°C derived from the PTx measurements are: $G^E = -710$ J/mol, $H^E = -4400$ J/mol, $TS^E = -3690$ J/mol, and $S^E = -10.2$ J/K-mol ($TS^E = H^E - G^E$). Malesinski [11] has classified binary mixtures according to the signs of their excess functions. He relates this classification to the like interactions (1-1, 2-2) and unlike (1-2) interactions of the two different molecules in solution. Systems where G^E , H^E , and TS^E are all negative include acetone + chloroform and water + hydrazine; the prevailing effect is that (1-2) intermolecular association due to hydrogen-bonding is greater than either the (1-1) or (2-2) hydrogen-bonding in the pure components. The system water + Me-EDA falls into this category.

At 90°C, the C_p^E is about 18.8 J/K-mol (by linear extrapolation of the data in Table 4) compared to the $S^E = -10.2$ J/K-mol. This is consistent with the finding by Abbott, et al., in their classification of excess function data [12] which shows that if $S^E < 0$, then

$C_p^E > 0$ for about 93% of the mixtures surveyed. Abbott, et al., also found that the absolute value of C_p^E is usually larger than the absolute value of S^E .

Figure 3 shows the bubble point temperature vs. composition (T_x) data from Table 1 for each of the six pressures studied. Note that a maximum boiling azeotrope exists at pressures of 13.3 and 26.7 kPa while at pressures of 53.3 kPa and above, the azeotrope has disappeared. At the intermediate isobar, 40.0 kPa, the T_x curve is nearly horizontal at compositions out to 0.5 mole fraction. Closer examination of the measured T_x data at 40.0 kPa reveals a minimum about 0.16°C less than the boiling point of pure Me-EDA and maximum about 0.12°C greater than the minimum. These extrema suggest that a double azeotrope exists in this region. The same behavior is shown by isothermal x-y plots at 60°, 90°, and 100°C in Figure 4 (the y values are derived from a Barker's method analysis of the $P T_x$ data as in Table 2).

The conditions that lead to double (multiple) azeotropes have been analyzed previously [13-15]. What is required is an asymmetry in the molecular interactions in either or both the liquid and vapor phases vs. composition, i. e., the molecules must both "attract" and "repulse" in different regions of binary composition space of the liquid and/or vapor. The effect of the asymmetric molecular interactions is enhanced if the two molecules have similar vapor pressures but double azeotropy has been observed when the two pure component have different vapor pressures [16]. At 85°C, water and Me-EDA have a vapor pressure ratio of 1.6 which is large compared to previously observed double azeotropes.

A concern about the validity of the small magnitude temperature extrema at 40.0 kPa is the stated purity of the Aldrich Me-EDA: 95 mass %. Our own FID GC analysis

shows area % purity of 97.9 to 99.2 area % (depending on lot #). Also, GC-MS analysis shows that the impurities are amines (ethylenediamine, N,N-dimethylethylenediamine, N,N'-dimethylethylenediamine, and 1-methylimidazolidine) that are chemically similar to Me-EDA. However, confirmation of the existence of a double azeotrope at temperatures near 85°C requires further laboratory experiments on carefully purified Me-EDA. A definitive experiment would be to measure the composition of the coexisting phases directly in a re-circulating equilibrium still [17]. Additional confirmation could also be provided by distillations in a spinning-band column [13].

Finally, Figure 5 shows an x-y plot of VLE data [1,2] for water + EDA. Note the similarity with the data reported here for Me-EDA: although the x-y behavior in the water-rich end of the binary remains reasonably constant, the x-y behavior in the EDA-rich end of the curve changes dramatically as pressure (temperature) increases. Hirata, et al., [2] report that at pressures above about 180 kPa, the maximum-boiling azeotrope for water + EDA disappears.

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TABLE 1 PTx data for water(1) + N-methylethylenediamine(2)

z1	x1	T/°C	P/kPa	z1	x1	T/°C	P/kPa
0.0000	0.0000	61.79	13.332	0.0000	0.0000	96.40	53.329
0.1303	0.1309	62.29	13.332	0.1303	0.1300	95.93	53.329
0.2001	0.2016	62.74	13.332	0.2001	0.2002	95.81	53.329
0.2998	0.3017	63.30	13.332	0.2998	0.3002	95.70	53.329
0.4002	0.4020	63.83	13.332	0.4002	0.4005	95.56	53.329
0.5003	0.5011	64.25	13.332	0.5003	0.4998	95.30	53.329
0.6012	0.5991	64.24	13.332	0.6012	0.5984	94.71	53.329
0.7000	0.6945	63.03	13.332	0.7000	0.6953	93.31	53.329
0.8000	0.7931	59.64	13.332	0.8000	0.7944	90.36	53.329
0.9000	0.8958	54.81	13.332	0.9000	0.8964	86.16	53.329
1.0000	1.0000	51.66	13.332	1.0000	1.0000	83.00	53.329
0.0000	0.0000	78.00	26.664	0.0000	0.0000	108.33	79.993
0.1303	0.1305	78.15	26.664	0.1303	0.1296	107.37	79.993
0.2001	0.2010	78.36	26.664	0.2001	0.1997	107.03	79.993
0.2998	0.3010	78.62	26.664	0.2998	0.2997	106.62	79.993
0.4002	0.4013	78.87	26.664	0.4002	0.4000	106.21	79.993
0.5003	0.5005	78.98	26.664	0.5003	0.4994	105.75	79.993
0.6012	0.5988	78.67	26.664	0.6012	0.5982	104.96	79.993
0.7000	0.6949	77.35	26.664	0.7000	0.6954	103.50	79.993
0.8000	0.7938	74.20	26.664	0.8000	0.7948	100.66	79.993
0.9000	0.8961	69.66	26.664	0.9000	0.8966	96.66	79.993
1.0000	1.0000	66.48	26.664	1.0000	1.0000	93.54	79.993
0.0000	0.0000	88.47	39.997	0.0000	0.0000	115.75	101.325
0.1303	0.1302	88.31	39.997	0.1303	0.1294	114.43	101.325
0.2001	0.2005	88.32	39.997	0.2001	0.1993	113.98	101.325
0.2998	0.3006	88.39	39.997	0.2998	0.2993	113.34	101.325
0.4002	0.4009	88.43	39.997	0.4002	0.3996	112.74	101.325
0.5003	0.5001	88.33	39.997	0.5003	0.4991	112.16	101.325
0.6012	0.5986	87.83	39.997	0.6012	0.5980	111.26	101.325
0.7000	0.6951	86.48	39.997	0.7000	0.6954	109.77	101.325
0.8000	0.7942	83.45	39.997	0.8000	0.7950	106.98	101.325
0.9000	0.8963	79.09	39.997	0.9000	0.8967	103.11	101.325
1.0000	1.0000	75.93	39.997	1.0000	1.0000	100.03	101.325

TABLE 2

Antoine equation constants and derived Pxy data at 90°C for water(1) + N-methylethylenediamine(2)

x_1 (90°C)	$A(x_1)$	$B(x_1)$	$C(x_1)$	P/kPa (90°C)	$y_1(\text{calc})$ (90°C)
0.0000	6.2494490	1332.558	198.257	42.329	0.0000
0.1302	6.6967420	1547.054	215.358	42.695	0.1390
0.2004	6.7245130	1536.514	211.641	42.723	0.2095
0.3004	7.0130070	1674.982	221.168	42.670	0.3001
0.4006	7.2048800	1755.098	224.830	42.671	0.3951
0.4998	7.1053990	1657.870	212.931	42.918	0.5117
0.5984	7.0932780	1621.006	207.361	43.850	0.6560
0.6951	7.0657220	1595.253	205.497	46.471	0.8034
0.7942	7.2330860	1716.080	221.306	52.549	0.9186
0.8963	7.2554890	1765.376	233.167	62.052	0.9794
1.0000	7.0781770	1658.430	226.918	70.014	1.0000

$\text{Log } P(x_1) = A(x_1) - B(x_1)/[t+C(x_1)]$; log = base 10, $P(x_1)$ = kPa, t = °C

TABLE 3

Redlich-Kister G^E parameters (J/mol) at 90°C for water(1) + N-methylethylenediamine(2)

# parm.	A	B	C	D	P rms error (kPa)
0	0.0				9.58
1	-783.02				3.10
2	-718.17	-620.80			0.500
3	-684.84	-595.55	-172.22		0.285
4	-679.07	-649.29	-213.30	149.88	0.229

TABLE 4

Excess heat capacity data for equimolar water(1) + N-methylethylenediamine(2) from differential scanning calorimetry, $C_p \cong C_\sigma$

T (°C)	C_p Water (J/mol-K)	C_p Me-EDA (J/mol-K)	C_p $x_1 = 0.5$ (J/mol-K)	C_p , Ideal $x_1 = 0.5$ (J/mol-K)	C_p^E $x_1 = 0.5$ (J/mol-K)
25	75.9	215.2	152.2	145.6	6.7
30	76.1	215.8	153.2	146.0	7.3
35	76.2	215.9	154.3	146.1	8.2
40	76.3	216.3	155.5	146.3	9.2
45	76.2	216.5	156.7	146.4	10.3
50	75.9	216.4	158.4	146.2	12.2
55	76.0	216.7	159.2	146.3	12.9
60	75.9	217.9	160.2	146.9	13.3
65	76.0	218.0	161.0	147.0	14.1
70	75.9	218.7	162.5	147.3	15.2
75	76.1	218.2	163.2	147.2	16.0
80	76.3	219.3	164.3	147.8	16.5

FIGURE CAPTIONS

Figure 1. Heat capacity (C_p) data for water, N-methylethylenediamine, and an equimolar mixture measured by differential scanning calorimetry.

Figure 2. Equimolar G^E/T vs. temperature for water(1) + N-methylethylenediamine(2).

Figure 3. Bubble point (T_x) data vs. composition for water(1) + N-methylethylenediamine(2) for the six measured isobars.

Figure 4. Vapor-liquid equilibrium (x-y) data for water(1) + N-methylethylenediamine(2) at 60°C, 90°C, and 100°C; data smoothed with a cubic spline.

Figure 5. Vapor-liquid equilibrium (x-y) data for water(1) + ethylenediamine(2) at 13.3 kPa, 101.325 kPa, and 179.3 kPa; data smoothed with a cubic spline.

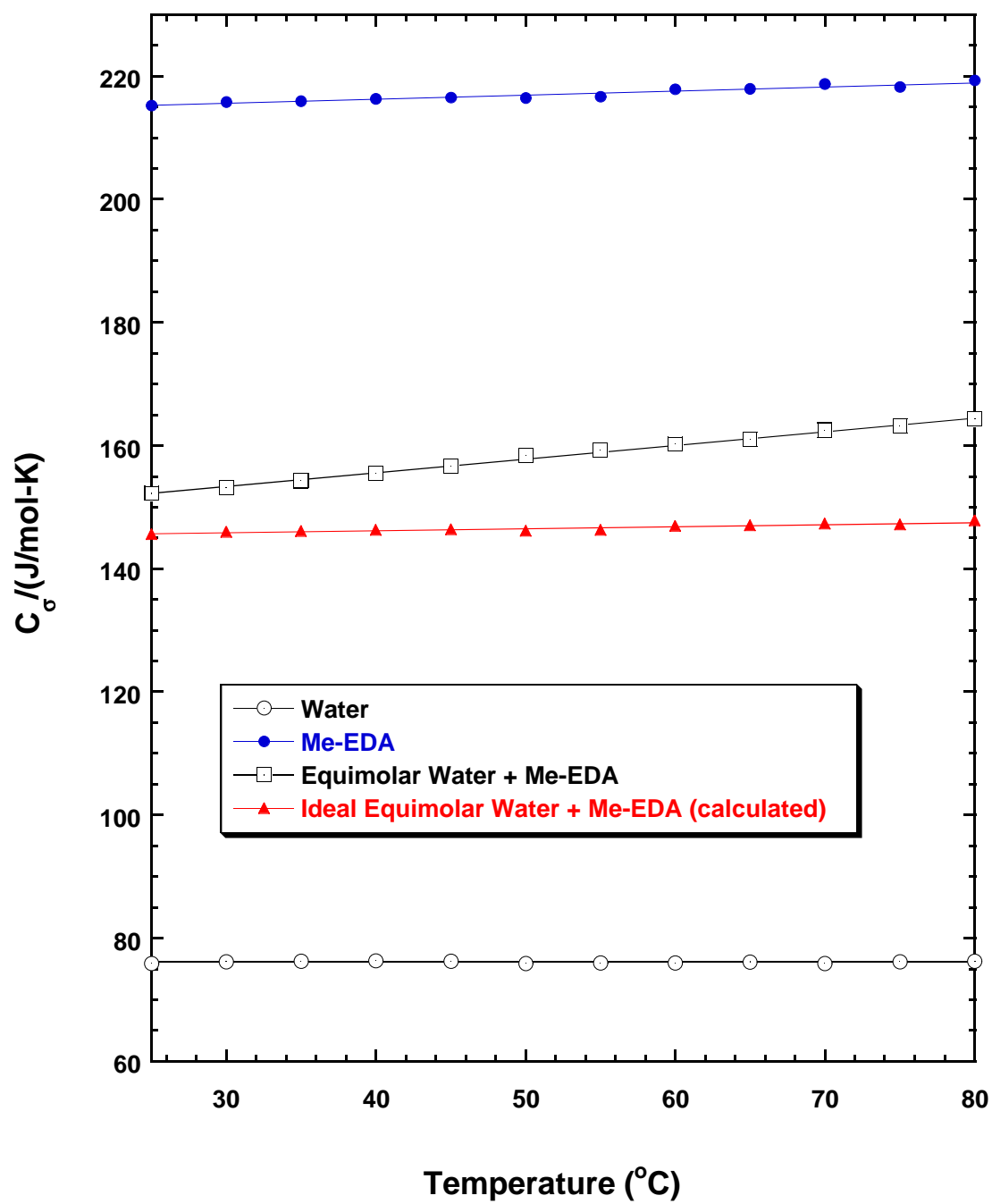


Figure 1 - Olson

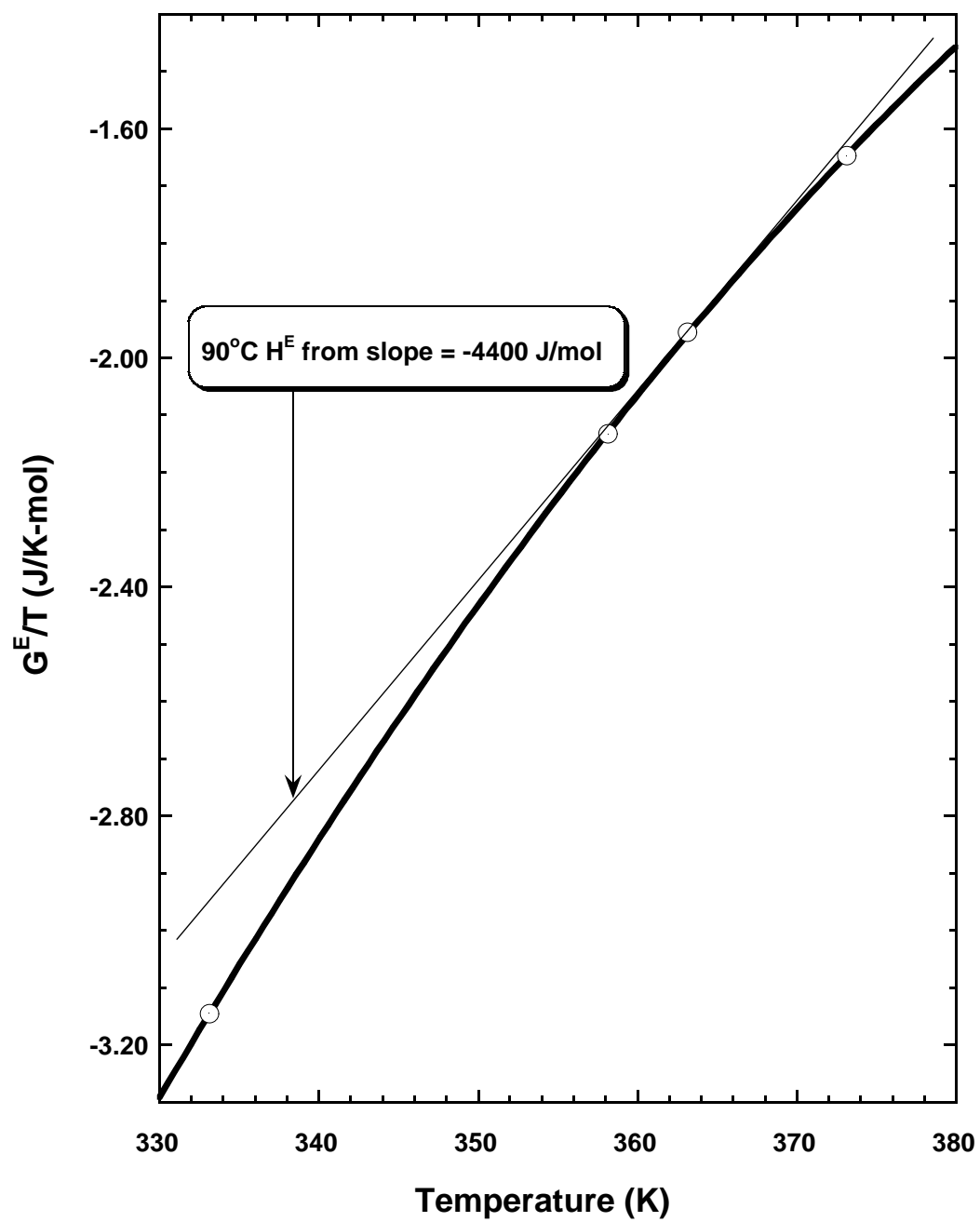


Figure 2 - Olson

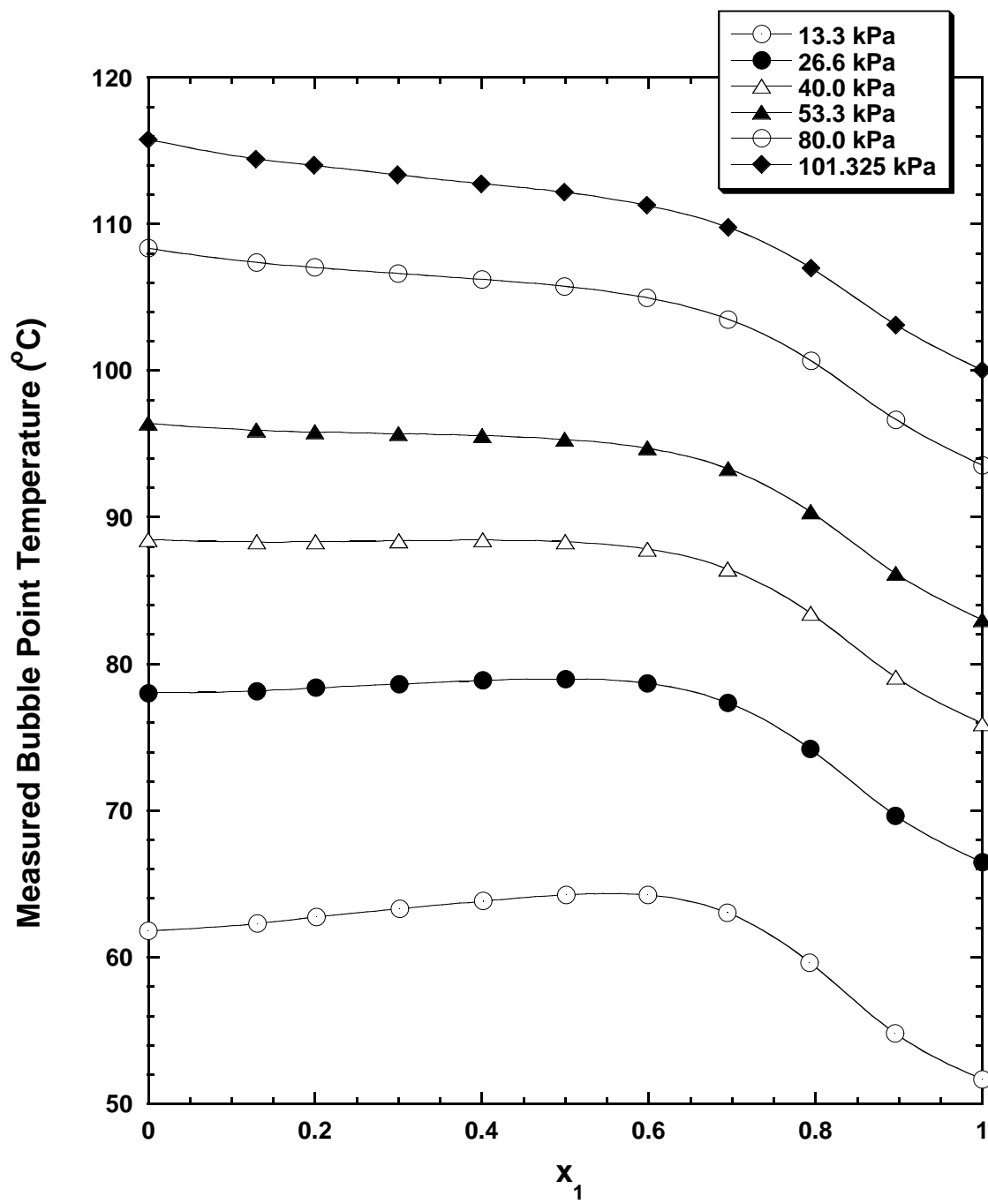


Figure 3 - Olson

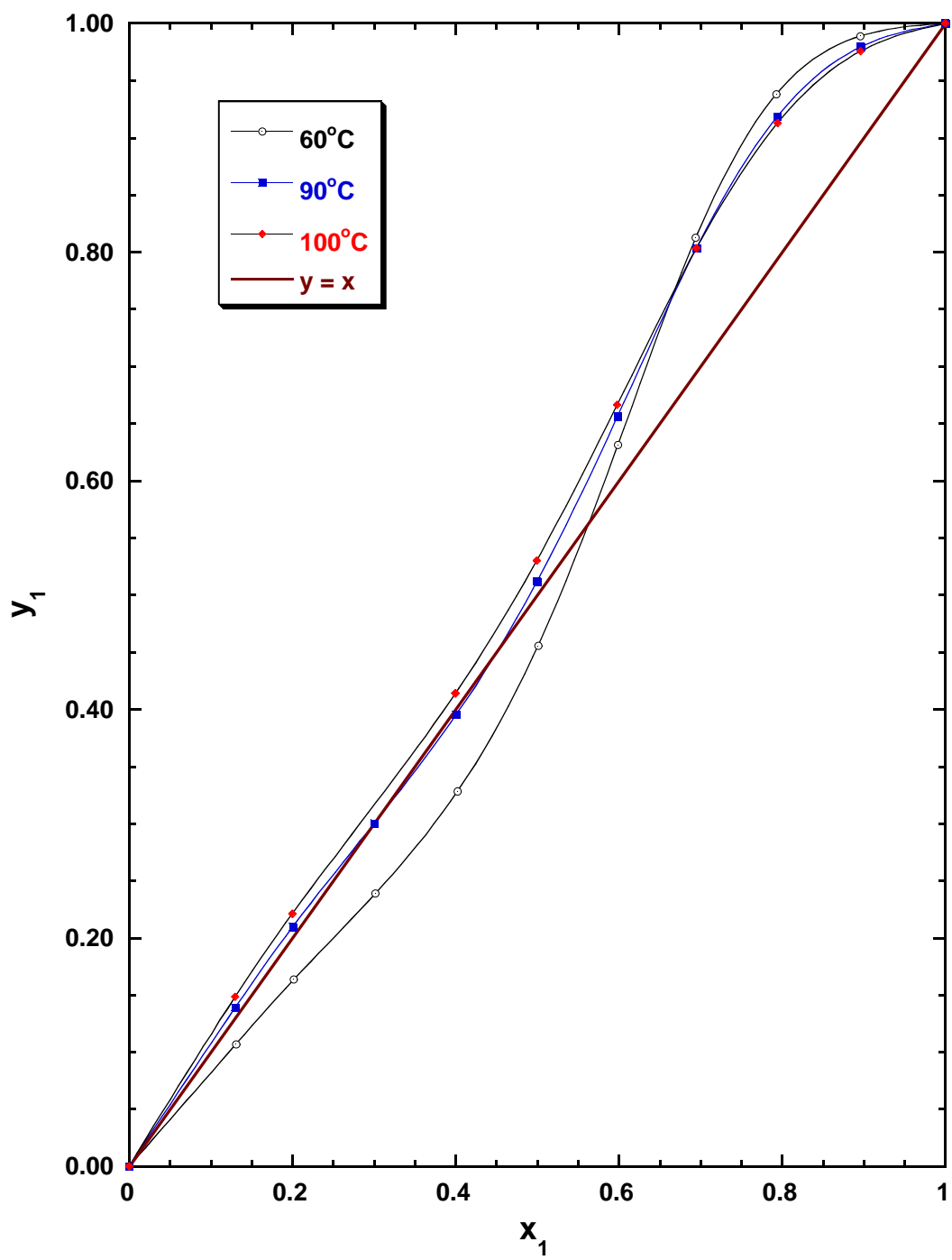


Figure 4 - Olson

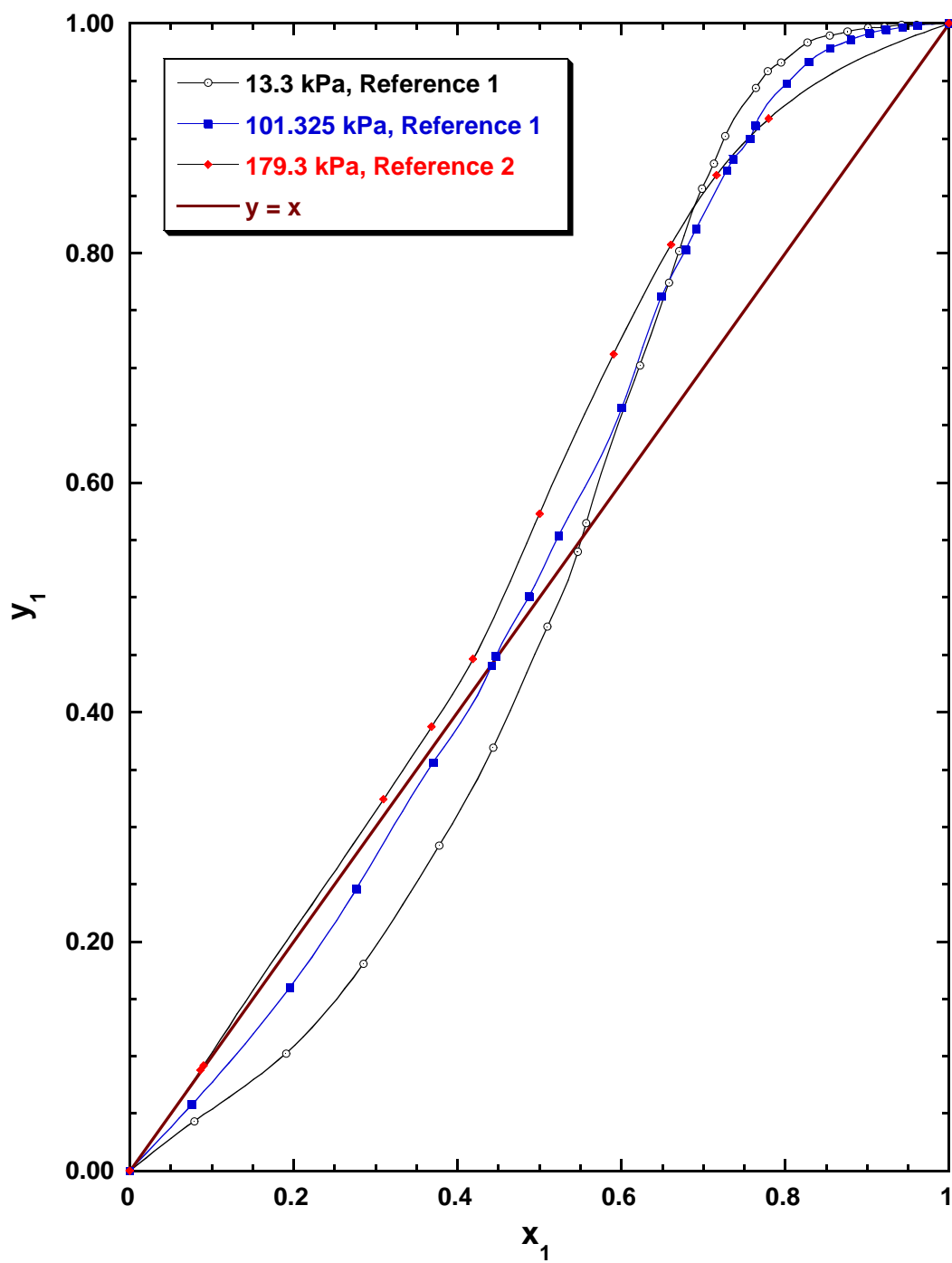


Figure 5 - Olson